REMOVAL AND RECOVERY OF PHOSPHORUS FROM MUNICIPAL WASTEWATER BY ADSORPTION COUPLED WITH CRYSTALLIZATION

By

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A Dissertation

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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DEDICATION

To my dearest husband, daughter and son

for their love and inspiration

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURES

Symbol	Description	Unit
A	Bed cross-sectional area	cm^2
Å	Angstrom	
AER	Adsorbent exhaustion rate	g/L
Al^{3+}	Aluminum (III) ion	
As	Arsenic	
BOD_5	Biochemical oxygen demand after 5 days	mg/L
BV	Bed volume	cm^3
C_b	Phosphorus concentration at breakthrough time	mg/L
C_o	Initial concentration of phosphorus	mg/L
C_t	Concentration of phosphorus at time t	mg/L
Ca^{2+}	Calcium ion	
$CaCO_3$	Calcium carbonate	
CaO	Calcium oxide	
$Ca(OH)_2$	Calcium hydroxide	
$Ca_3(PO_4)_2$	Tricalcium phosphate	
Cd	Cadmium	
Cl^-	Chloride ion	
ClO_4^-	Perchlorate ion	
CO_2	Carbon dioxide	
CO_3^{2-}	Carbonate ion	
COD	Chemical oxygen demand	mg/L
Cu^{2+}	Copper ion	
D	Column inner diameter	cm

DMF	N,N-dimethylformamide	
E	Activation energy	kJ/mol
EBCT	Empty bed contact time	min
EDA	Ethylene diamine triethylamine	
EDTA	Ethylene diamine tetra acetic acid	
F^-	Fluoride ion	
Fe^{2+}	Iron (II) ion	
Fe^{3+}	Iron (III) ion	
g/L	Gram per liter	
HCl	Hydrochloric acid	
Hg	Mercury	
HNO_3	Nitric acid	
H_3PO_4	Phosphoric acid	
$H_2PO_4^-$	Di hydrogen phosphate ion	
HPO_4^{2-}	Hydrogen phosphate ion	
H_2SO_4	Sulfuric acid	
IS	Ionic strength	M
k_{AB}	Adams-Bohart kinetic constant	L/mg.min
K_F	Freundlich constant	$(mg/g)(L/mg)^{1/n}$
K_L	Langmuir constant related to the energy of adsorption	L/mg
k_{Th}	Thomas rate constant	mL/min.mg
k_{YN}	Yoon-Nelson rate velocity constant	1/min
KCl	Potassium chloride	
m	Mass of dry adsorbent	g
m^2/g	Square meter per gram	
m^3	Cubic meter	
m^3/d	Cubic meter per day	
kg/d	Kilogram per day	
km^3	Cubic kilometer	
m_f	Mass of empty flask	
m_{f+w}	Mass of filled volumetric flask + water	
m_{s+f}	Mass of ZLO + volumetric flask	
m_{s+f+w}	Mass of ZLO + volumetric flask + water	
Mg^{2+}	Magnesium ion	
$MgCl_2$	Magnesium chloride	
$MgCl_2.6H_2O$	Magnesium chloride hexahydrate	

$MgNH_4PO_4.6H_2O$	Magnesium ammonium phosphate hexahydrate	
MgO	Magnesium oxide	
$Mg(OH)_2$	Magnesium hydroxide	
$MgSO_4.7H_2O$	Magnesium sulfate heptahydrate	
mg/L	Milligram per liter	
mg P/L	Milligram phosphorus per liter	
mg PO_4/g	Milligram phosphate per gram	
min	Minute	
mL/min	Milliliter per minute	
MoO_4^{-2}	Molybdate ion	
MPa	Mega Pascal	
MSBG	Modified sugarcane baggase	
µm	Micrometer	
µM	Micro molar	
mM	Mill molar	
Mn	Manganese	
mV	mill volt	
n	Freundlich constant	
N	Nitrogen	
NaOH	Sodium hydroxide	
Na_2HPO_4	Disodium hydrogen phosphate	
$NaH_2PO_4.2H_2O$	Sodium dihydrogen orthophosphate dihydrate	
$Na_{3.25}(OH)_{0.25}PO_4.12H_2O$	Trisodium phosphate dodecahydrate	
NH_4^+	Ammonium ion	
NH_4Cl	Ammonium chloride	
Ni^{2+}	Nickel ion	
NO_2^-	Nitrite ion	
NO_3^-	Nitrate ion	
N_o	Saturation phosphorus concentration	mg/L
NTUs	Nephelometric turbidity units	
P	Phosphorus	
Pb^{2+}	Lead ion	
P_s	Particle size	mm
PO_4^{3-}	Phosphate ion	
Q	Volumetric flow rate	mL/min
q_b	Amount of phosphorus adsorbed per unit of dry	mg/g

	weight of adsorbent at breakthrough time	
q_e	Equilibrium adsorption capacity of the adsorbent	mg/g
q_m	Maximum adsorption capacity of the adsorbent	mg/g
q_s	Amount of phosphorus adsorbed per unit of dry weight of adsorbent at saturation time	mg/g
q_{total}	Total mass of phosphorus adsorbed	mg
R_b	Removal percentage of phosphorus at breakthrough time	%
R_s	Removal percentage of phosphorus at saturation time	%
rpm	Revolutions per minute	
SBG	Sugarcane baggase	
SO_4^{2-}	Sulfate ion	
SeO_3^{2-}	Selenite ion	
t	Service time of the column	min
t_b	Service time at breakthrough point	min
t_s	Service time at saturation point	min
TOC	Total organic carbon	mg/L
TSS	Total suspended solids	mg/L
V_b	Volume of water treated at breakthrough time	L
V_e	Volume of water treated at exhaustion time	L
V_s	Superficial velocity	cm/min
VO_3^-	Vanadate ion	
Z	Bed height	cm
Z_o	Critical bed depth	cm
Zn^{2+}	Zinc ion	
Zr^{4+}	Zirconium ion	
$ZrOCl_2.8H_2O$	Zirconyl chloride octahydrate	
ΔG	Change in Gibbs free energy	J/mol
ΔH	Change in enthalpy	J/mol
ΔS	Change in entropy	J/mol/K
$	United States dollar	
€	Euro	

ABBREVIATIONS

Symbol	Description
ATP	Adenosine tri phosphate
AWBs	Agricultural wastes/by-products
BDST	Bed depth service time
BET	Brunauer emmett teller
BSR	Batch stirred reactor
DNA	Deoxyribonucleic acid
FTIR	Fourier transform infrared spectroscopy
HAP	Hydroxyapatite
ILO	Iron loaded okara
ISSA	Incinerated sewage sludge ash
IZLO	Iron/zirconium loaded okara
MAP	Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$)
MBR	Membrane bioreactor
MTZ	Mass transfer zone
NOM	Natural organic matter
PAOs	Polyphosphate accumulating organisms
PBR	Packed bed reactor
PHB	Poly hydroxyl butyrate
ppm	Part per million
RNA	Ribonucleic acid
RO	Reverse osmosis
SEM-EDS	Scanning electron microscopy with X-ray microanalysis
TEM	Transmission electron microscope
USEPA	United States environmental protection agency

WWTP	Waste water treatment plant
XRD	Powder X-ray diffraction
ZLO	Zirconium loaded okara

GREEK SYMBOLS

Symbol	Description	Unit
τ	The time required for 50% phosphorus breakthrough	min
ρ_b	Bulk density of the adsorbent	g/cm^3
ρ_p	Particle density of the adsorbent	g/cm^3
ρ_w	Density of water	g/cm^3
η	Porosity of the adsorbent	%

PhD DISSERTATION ABSTRACT

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Abstract:

Phosphorus is both critical and detrimental so it is desirable to develop a process that can not only remove but also recovery phosphorus. As the global phosphate reserve will be exhausted in 50-100 years, there is a need to explore alternatives to phosphate ores. Municipal wastewater is a significant source of phosphorus for recovery due to extremely high volumes and low levels of hazardous substances. This study investigates the feasibility of removing and recovering phosphorus from municipal wastewater by adsorption coupled with crystallization. Adsorbents were prepared from soybean by-product (okara) using metal loading method. The results indicated that zirconium loaded okara (ZLO) was the best among three developed adsorbents. The maximum adsorption capacity of ZLO was 58.93 mg PO_4/g adsorbent. The rapid adsorption was observed with 95% of the removal efficiency in 30 min. Isotherm data was best fitted by Freundlich model while kinetic data was satisfactorily described by Pseudo-second order model. Thermodynamic results revealed that the adsorption was feasible, spontaneous, and endothermic. The solution pH did not affect PO_4^{3-} uptake in a wide range of 2-11. CO_3^{2-} had a profound effect on PO_4^{3-}retention, whereas SO_4^{2-}, NO_3^- and

Cl^- were trivial inhibitors. Successful desorption and regeneration were achieved with 0.2 M NaOH and 0.1 M HCl, respectively. The ligand exchange was an important pathway for PO_4^{3-} capture by ZLO. The column results showed that the highest dynamic adsorption capacity of ZLO was 50.35 mg PO_4/g adsorbent. Thomas and Bed depth service time (BDST) models were most suitable for the description of the column adsorption behavior. ZLO column could be recycled at least three cycles with a reduction of 18.64% and 8.7% of adsorption capacity and adsorbent weight, respectively. A semi-pilot scale column packed with 100 g ZLO was capable of treating 132.5 L of municipal wastewater to meet the recommended discharge standard (1 mg P/L). The Zr^{4+} detachment from ZLO during its operation was negligible. The struvite (MAP - Magnesium ammonium phosphate hexahydrate - $MgNH_4PO_4.6H_2O$) recovery from desorption solution was most favored at pH 9, Mg: N: P molar ratio of 2:2:1, room temperature, using a combination of $MgCl_2.6H_2O$ and NH_4Cl. The harvested MAP was characterized by 93% MAP and 89% by mass P-bioavailability. Overall, the removal and recovery of phosphorus from municipal wastewater can be achieved by means of adsorption and crystallization. However, further study is necessary to make the process more economically viable.

Graphical Abstract